AD-A277 003

# ...NTATION PAGE

Form Approved
OMB No. 0704-0188

...ated to average 1 hour per response including the time for reviewing instructions searching existing data sources ... reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this ... burden to Washington Headquarters Services, Directorate for Information Operations and Reports, 1215 Jefferson ... Office of Management and Budget, Paperwork Reduction Project (0704-0188) Washington DC 20503

| ...ORT DATE | 3. REPORT TYPE AND DATES COVERED |
|---|---|
| March 1994 | Interim, 1 July 1992 - 1 March 1994 |

**4. TITLE AND SUBTITLE**

Tetraalkyldiarsines as Potential Precursors for Electronic Materials: Synthesis and Characterization of Various *Iso*-Propyl Arsenic Compounds

**5. FUNDING NUMBERS**

G: N00014-92-J-1828
R&T PR: 44135035—01

**6. AUTHOR(S)**

Lawrence F. Brough, Liu Gang, Matthew A. Lipkovich, Thomas J. Colacot, Virgil L. Goedken, and William S. Rees, Jr.

**7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)**

School of Chemistry and Biochemistry and
School of Materials Science and Engineering
Georgia Institute of Technology
Atlanta, Georgia 30332-0400

**8. PERFORMING ORGANIZATION REPORT NUMBER**

TR No. 4

**9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)**

Department of the Navy
Office of the Chief of Naval Research
Arlington, Virginia 22217-500



**10. SPONSORING/MONITORING AGENCY REPORT NUMBER**

unknown

**11. SUPPLEMENTARY NOTES**

Accepted for Publication in: *Materials Research Society Proceedings*.

**12a. DISTRIBUTION/AVAILABILITY STATEMENT**

This document has been approved for public release and sale; its distribution is unlimited.



9PY

**13. ABSTRACT** *(Maximum 200 words)*

*Tetrakis*(*iso*-propyl)diarsine was synthesized by the reaction of ($i$-Pr)AsLi with $(i\text{-Pr})_2$AsI. The lithium salt of the secondary arsine was produced following deprotonation of $(i\text{-Pr})_2$AsH, obtained by reduction of $(i\text{-Pr})_2$AsI, which was prepared by the thermolysis of $(i\text{-Pr})_3AsI_2$. The X-ray crystal structure of $[(i\text{-Pr})_3\text{AsI}][\text{I}]$ has been determined on the product of the reaction of $(i\text{-Pr})_3$As and $I_2$. Compounds of the general form E=As($i$-Pr)$_3$ (E = O, S, Se) have been prepared.

| 14. SUBJECT TERMS | 15. NUMBER OF PAGES |
|---|---|
| organoarsenic chemistry, *iso*-propyl arsenic compounds, diarsines | 9 |
| | 16. PRICE CODE |

| 17. SECURITY CLASSIFICATION OF REPORT | 18. SECURITY CLASSIFICATION OF THIS PAGE | 19. SECURITY CLASSIFICATION OF ABSTRACT | 20. LIMITATION OF ABSTRACT |
|---|---|---|---|
| Unclassified | Unclassified | Unclassified | UL |

OFFICE OF NAVAL RESEARCH

GRANT N00014-92-J-1820

R&T Code 4135035---01

Technical Report No. 4

# Tetraalkyldiarsines as Potential Precursors for Electronic Materials: Synthesis and Characterization of Various *Iso*-Propyl Arsenic Compounds

by

Lawrence F. Brough, Liu Gang, Matthew A. Lipkovich, Thomas J. Colacot,
Virgil L. Goedken, and William S. Rees, Jr.

Accepted for Publication
in

*Materials Research Society Proceedings*

School of Chemistry and Biochemistry and
School of Materials Science and Engineering
Georgia Institute of Technology
Atlanta, Georgia 30332-0400

8 March 1994

# Tetraalkyldiarsines as Precursors in the Synthesis of Electronic Materials: Synthesis and Characterization of Various *iso*-Propyl Arsenic Compounds


Lawrence F. Brough, Liu Gang, Matthew A. Lipkovich,
Thomas J. Colacot, Virgil L. Goedken, and William S. Rees, Jr.*
Department of Chemistry
and Materials Research and Technology Center
The Florida State University
Tallahassee, Florida 32306-3006
VOICE: 904-644-4768
FAX: 904-644-8281



Fall Meeting of the Materials Research Society
Boston, MA

Symposium W

Manuscript Number: W 2.8

# TETRAALKYLDIARSINES AS POTENTIAL PRECURSORS FOR ELECTRONIC MATERIALS: SYNTHESIS AND CHARACTERIZATION OF VARIOUS *ISO*-PROPYL ARSENIC COMPOUNDS

LAWRENCE F. BROUGH, LIU GANG, MATTHEW A. LIPKOVICH, THOMAS J. COLACOT, VIRGIL L. GOEDKEN,‡ AND WILLIAM S. REES, JR.
Department of Chemistry and Materials Research and Technology Center, The Florida State University, Tallahassee, Florida 32306-3006

## ABSTRACT

*Tetrakis*(*iso*-propyl)diarsine was synthesized by the reaction of $(i\text{-Pr})_2AsLi$ with $(i\text{-Pr})_2AsI$. The lithium salt of the secondary arsine was produced following deprotonation of $(i\text{-Pr})_2AsH$, obtained by reduction of $(i\text{-Pr})_2AsI$, which was prepared by the thermolysis of $(i\text{-Pr})_3AsI_2$. The X-ray crystal structure of $[(i\text{-Pr})_3AsI][I]$ has been determined on the product of the reaction of $(i\text{-Pr})_3As$ and $I_2$. Compounds of the general form $E{=}As(i\text{-Pr})_3$ (E = O, S, Se) have been prepared.

## INTRODUCTION

Several recent publications have discussed the potential of utilizing *tetrakis*(alkyl)diarsines as *in situ* sources of arsenic for employment in the preparation of arsenic-containing electronic materials.[1] Such routes to, for example, GaAs presently rely on toxic and highly volatile precursors (*e.g.*, $AsH_3$). The motivation for this new approach is depicted in equation 1. Although the molecularity of the arsenic-containing product is uncertain, such routes have seen some moderate success. The precise stoichiometry of the reaction product may be 1/2 ($As_4$) or 2 As; however, the confirmation of this synthetic procedure for *in situ* generation of elemental arsenic-containing species relies less on the accretion coefficient, and more on the lack of any carbon-containing species in the product. Such contamination by the disadvantageous decomposition of pendant organic groups highly is detrimental to the final electronic properties of such materials.

‡Deceased 22 December 1992

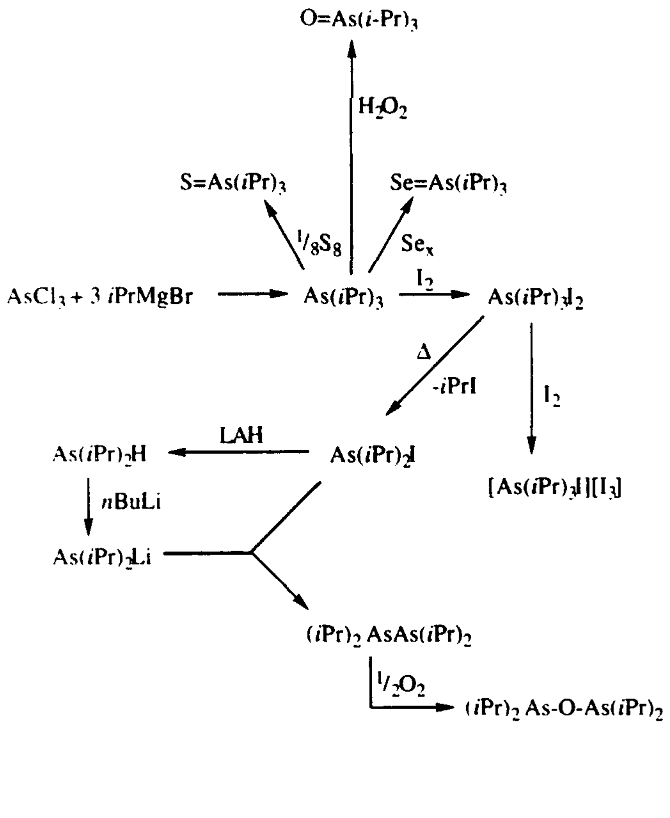
*Address all correspondence to this author at: School of Chemistry and Biochemistry and School of Materials Science and Engineering, Georgia Institute of Technology, Atlanta, Georgia 30332.

As one component of a program directed at an examination of the generality of this approach,[1c] several *iso*-propyl arsenic compounds have been prepared. The synthesis and characterization of some of these organometallic compounds is reported in this contribution.

$$3\ R_2As\text{-}AsR_2 \rightleftharpoons 4\ AsR_3 + As_2 \qquad (1)$$

## RESULTS AND DISCUSSION

Credit is given to Cadet for the initial report of a compound containing a metal-carbon bond.[2] His 1760 paper describes the simplest tetraalkyldiarsine, $(H_3C)_2As\text{-}As(CH_3)_2$, given the trivial name of cacodyl. A variety of methods have been developed over the years for the preparation of diarsines.[3] In order to address the above-described motivation for exploration of tetraalkyldiarsines as potential precursors in the OMVPE growth of high-quality semiconducting materials, *tetrakis*(*iso*-propyl)diarsine was prepared (Scheme I).




Scheme I

## Crystal structures of $[(i\text{-Pr})_3AsI][I]$ and $[(i\text{-Pr})_3AsI][I_3]$

The general format for the oxidative addition of a dihalogen molecule to a tertiary organoarsine (equation 2) can proceed according to two alternate pathways.

$$R_3As + X_2 \begin{cases} \xrightarrow{\textbf{Route A}} R_3AsX_2 \\ \xrightarrow{\textbf{Route B}} [R_3AsX][X] \end{cases} \qquad (2)$$

In Route A, the ~$T_d$ $R_3As$ is transformed into the molecular $R_3AsX_2$ with a trigonal bipyramidal geometry. In Route B, the resultant product is an [arsonium][halide] ionic moiety. Factors influencing the path of choice include the electronic and spatial considerations of the alkyl groups represented in the tertiary arsine, as well as the $\Delta\chi$ present between the halogen and arsenic. For example, both $[Me_3PX][X]$ and $Me_3SbX_2$ have been characterized.[4] In all likelyhood, the difluorides are covalently bound. Previous infrared spectroscopic work has indicated that $R_3AsI_2$ compounds (R = Me, Et) are ionic in the solid state.[5] In the present investigation, $[(i\text{-Pr})_3AsI][I]$ was determined, by X-ray diffraction, to be the conformation adopted by the reaction product of $(i\text{-Pr})_3As$ and $I_2$. If the stoichiometry was not carefully controlled (equation 3), a different product was obtained. There have been reports of comparable reactions observed for $Ph_3As$.[6]

$$[(i\text{-Pr})_3AsI][I] + I_2 \longrightarrow [(i\text{-Pr})_3AsI][I_3] \qquad (3)$$

A single crystal structure determination also was conducted on $[(i\text{-Pr})_3AsI][I_3]$. It was, however, suspended prior to complete refinement. Once the identical atomic linkages were ascertained to be present in the organometallic cation, the structural refinement was not pursued further. There was little new structural information revealed in the anion replacement species.

Pertinent crystal and refinement data along with selected interatomic distances and angles will be published elsewhere. An ORTEP representation of the structure is presented (Figure 1), including both covalent and ionic interactions between As and I atoms.

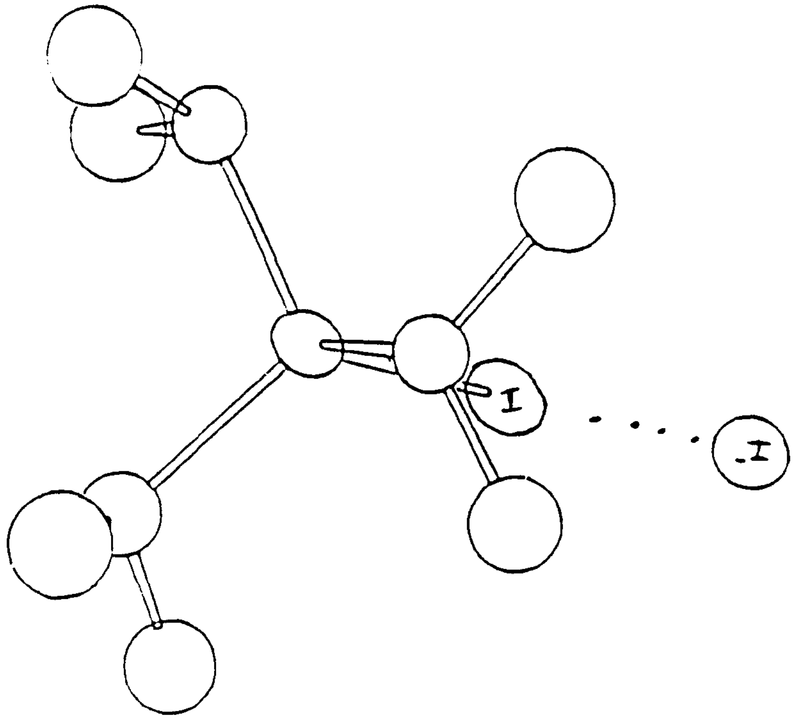



Figure 1 ORTEP representation of [(*i*-Pr)3AsI][I]
Open circles represent Carbon atoms. Hydrogen
atoms have been omitted for clarity of presentation.

<u>Preparation of E=As(*i*-Pr)$_3$ (E = O, S, Se)</u>

The preparation of O=As(*i*-Pr)$_3$ was effected under mild conditions (equation 4).

$$\mathrm{As}(i\text{-Pr})_3 + {}^1/_2\,\mathrm{H_2O_2} \longrightarrow \mathrm{O{=}As}(i\text{-Pr})_3 \qquad (4)$$

Either a solvent-mediated or a direct reaction can be utilized in the synthesis of S=As(*i*-Pr)$_3$ (equation 5 - 6).

$$ {}^1/_8\,\mathrm{S_8} + \mathrm{As}(i\text{-Pr})_3 \xrightarrow[\mathrm{N_{2(g)}},\ 18\ \mathrm{h}]{\mathrm{THF,\ r.t.}} \mathrm{S{=}As}(i\text{-Pr})_3 \qquad (5)$$

$$ {}^1/_8\,\mathrm{S_8} + \mathrm{As}(i\text{-Pr})_3 \xrightarrow[100^\circ\mathrm{C}]{\mathrm{neat}} \mathrm{S{=}As}(i\text{-Pr})_3 \qquad (6)$$

The most efficient route for the preparation of $Se{=}As(i\text{-}Pr)_3$ was determined to be the reaction of $As(i\text{-}Pr)_3$ with elemental selenium (equation 7).

$$As(i\text{-}Pr)_3 + {}^{1}/_{x}\, Se_x \xrightarrow[10\ \text{min}]{150°C} Se{=}As(i\text{-}Pr)_3 \qquad (7)$$

## ACKNOWLEDGEMENTS

We acknowledge support of this project by the Office of Naval Research Chemistry Division. L.F.B. was the recipient of a Florida State University Summer Faculty Professional Enhancement Program stipend during the summer of 1990.

## REFERENCES

1. a) C. W. Porter and P. Borgstrom, J. Am. Chem. Soc. **41**, 2048 (1919). b) Wide Gap II-VI Semiconductors, W. Kuhn, H. P. Wagner, H. Stanzi, K. Wolf, K. Worle, S. Lankes, J. Betz, M. Woraz, D. Lichtenberger, H. Leiderer, W. Gebhard and R. Triboulet, R. L. Aulombard and J. B. Mullin, eds., (Adam Hilger, Bristol, UK), 1991, p. A105. c) V. L. Goedken, L. F. Brough and W. S. Rees, Jr., J. Organomet. Chem. **449**, 125 (1993).
2. C. Elschenbroich and A. Salzer, Organometallics: A Concise Introduction, (VCH, New York), 1992.
3. G. O. Doak and L. D. Freedman, Organometallic Compounds of Arsenic, Antimony, and Bismuth, (Wiley-Interscience, New York), 1970.
4. a) J. Goubeau and R. Baumgärtner, Z. Electrochem. **64**, 598 (1960). b) E. F. Wells, Z. Kristallogr. **99**, 367 (1938).
5. a) M. H. O'Brien, G. O. Doak, and G. G. Long, Inorg. Chim. Acta **1**, 34 (1967). b) M. H. O'Brien, Ph.D. Thesis, North Carolina State University, 1968.
6. a) K. R. Bhaskar, S. N. Bhat, S. Singh, and C. N. R. Rao, J. Inorg. Nucl. Chem. **28**, 1915 (1966). b) S. N. Bhat and C. N. R. Rao, J. Amer. Chem. Soc. **88**, 3216 (1966).

## TECHNICAL REPORT DISTRIBUTION LIST - GENERAL

Office of Naval Research (2)*
Chemistry Division, Code 1113
800 North Quincy Street
Arlington, Virginia 22217-5000

Dr. James S. Murday (1)
Chemistry Division, Code 6100
Naval Research Laboratory
Washington, D.C. 20375-5000

Dr. Robert Green, Director (1)
Chemistry Division, Code 385
Naval Air Weapons Center
Weapons Division
China Lake, CA 93555-6001

Dr. Elek Lindner (1)
Naval Command, Control and Ocean
Surveillance Center
RDT&E Division
San Diego, CA 92152-5000

Dr. Bernard E. Douda (1)
Crane Division
Naval Surface Warfare Center
Crane, Indiana 47522-5000

Dr. Richard W. Drisko (1)
Naval Civil Engineering
Laboratory
Code L52
Port Hueneme, CA 93043

Dr. Harold H. Singerman (1)
Naval Surface Warfare Center
Carderock Division Detachment
Annapolis, MD 21402-1198

Dr. Eugene C. Fischer (1)
Code 2840
Naval Surface Warfare Center
Carderock Division Detachment
Annapolis, MD 21402-1198

Defense Technical Information
Center (2)
Building 5, Cameron Station
Alexandria, VA 22314

* Number of copies to forward